Band structure of CdS and CdSe at high pressure

Phillip Cervantes and Quentin Williams

Physics Department, University of California Santa Cruz, Santa Cruz, California 95064
and Department of Earth Sciences, University of California Santa Cruz, Santa Cruz, California 95064

Michel Côté, Oleg Zakharov, and Marvin L. Cohen

Department of Physics, University of California Berkeley, Berkeley, California 94720
and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

The indirect energy gaps of NaCl-structured CdS and CdSe are measured using absorption spectroscopy to approximately 55 and 42 GPa, respectively. The gaps shift linearly with pressure and their pressure dependence generally is in good agreement with previous measurements to 16 GPa. Also, band calculations using pseudo-potentials and density-functional theory are conducted on CdS as a function of pressure. The shift in the energy gap of CdS with pressure (dE_{gap}/dP) is experimentally determined to be $-5.7(6) \times 10^{-3}$ eV/GPa, in good agreement with the theoretical calculation of -5.6×10^{-3} eV/GPa. The pressure dependence of the gap of CdSe is measured to be $-4.0(2) \times 10^{-3}$ eV/GPa, while previous theoretical work yielded -6.0×10^{-3} eV/GPa. Relative to a previous experimental result on CdSe, our measured shift is in considerably closer agreement with theory. The energy gap in both materials is indirect throughout the pressure range of these measurements. There is also no compression-induced change in the location in k space of the valence-band maxima for either the experimental or theoretical results. In contrast to previous inferences for CdS, the gap appears to remain from the $\mathbf{L}$ point to the $\mathbf{X}$ point up to our maximum pressure. Based on a simple linear extrapolation of our data, we estimate the metallization pressures of NaCl-structured CdS and CdSe to be above 250 and 150 GPa, respectively. Because phase transitions occur in both materials below these pressures, it is unlikely that either of the NaCl-structured phases will undergo metallization. [S0163-1829(96)02948-7]

I. INTRODUCTION

The electronic band structures of CdS and CdSe under compression have been of interest since the pioneering study of Edwards and Drickamer.[1] Both of these materials convert to the NaCl structure from the lower-pressure wurtzite-structured phase at pressures near 3 GPa.[1–3] The energy gap between the valence and conduction bands of these NaCl-structured phases can be both determined and identified as direct or indirect by measuring the absorption spectrum of pressurized samples. Previously, the highest pressure at which such measurements had been conducted on CdS and CdSe were 16 and 5 GPa, respectively.[1] Here we present measurements of the CdS and CdSe energy gaps to 55 and 42 GPa, respectively. Additionally, we present theoretical calculations on CdS and compare our experimental data with previous theoretical results on CdSe.[4] These theoretical band calculations are demonstrated to be in good agreement with the experimental data.

Our principal concern is the pressure shift of the energy gap (dE_{gap}/dP) of the NaCl-structured phase of these two chalcogenides. This shift is useful for estimating the conditions under which metallization of these compounds might occur. In particular, whether the isoelectronic NaCl-structured Zn and Cd chalcogenides metallize under compression is an interesting issue. Based on conductivity measurements, NaCl-structured ZnSe has recently been observed to metallize near 15 GPa,[5] while the conductivity of CdSe indicates that it remains a semiconductor to pressures of at least 50 GPa.[6] This behavior is notable, as simple systemat-

ics suggest that the heavier members of an isoelectronic series tend to metallize at lower pressures.[7] For comparison, NaCl-structured HgSe appears to metallize between 16 and 21 GPa,[8] while ZnS in this structure has an indirect gap near 2 eV.[9,10]

Characterizing the pressure shift of band gaps also provides a particularly rigorous test of theoretical calculations of semiconductor band structures. Moreover, changes in band structure may also be manifested in changes of the slope of the energy gap versus pressure. In this regard, it has been proposed that the indirect gap of CdS may undergo a change in character from an $\mathbf{L} \rightarrow \mathbf{X}$ to a $\mathbf{\Sigma} \rightarrow \mathbf{X}$ transition at high pressures.[11] Here we evaluate, from both experimental and theoretical viewpoints, whether such a shift occurs in either CdS or CdSe.

II. EXPERIMENTS

Absorption spectra of the indirect gaps of NaCl-structured CdS and CdSe were measured using a modified Mao-Bell diamond-anvil cell equipped with type-I diamond anvils.[12] The samples used were powdered samples of 99.99% purity from Alfa-Ventron, Inc. A silicon diode detector was used to measure the absorption spectra of CdS in the frequency interval between 9000 and 15 000 cm^{-1} (1.1–1.9 eV), while an InSb detector was used to characterize the CdSe absorption spectra between 2000 and 9000 cm^{-1} (0.2–1.1 eV). All spectra were measured using a Bruker IFS-66V Fourier transform infrared spectrometer and are reported with a resolution of 4 cm^{-1}.

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A preindented inconel gasket with an approximately 200-μm-diam hole was used to contain the sample between diamonds with 350-μm-diam culets. The powdered samples were loaded into the hole with multiple grains of ruby powder placed on top of the samples. Pressure measurements were made using the well-known ruby fluorescence technique.[13–15] For CdSe, no pressure medium was used, while for our CdS, one sample contained a 16:3:1 mixture of methanol:ethanol:water, while another contained a small amount of argon as a pressure medium. The layer of CdS used in both runs was approximately 2–4 μm thick, while for CdSe, a layer approximately 10–15 μm in thickness was used.

Under transmitted light, NaCl-structured CdS is reddish orange. Dark red streaks appear within the sample at approximately 3 GPa during the phase transition from the wurtzite to the rocksalt structure. Such an effect has been previously observed[2,11] and is likely to be associated with defect production during the phase transition;[2] similar defect-induced heterogeneity in sample color has also been observed in ZnS,[9] CuBr, CuCl, and HI under pressure.[16,17] By using liquid pressure media, which reduced pressure gradients, this streaking was reduced, although not eliminated. Because of the relatively large band gaps of these materials, absorptions associated with the pressure media and ruby have no effect on our results.

III. RESULTS

The optical absorption spectrum of a semiconductor provides a straightforward way of determining its gap energy.[18] For substances with indirect energy gaps, it is predicted that the absorption spectrum will show a quadratic dependence on energy near the band edge; departures from such quadratic behavior are often associated with defect absorption. Ignoring defects, the absorption coefficient α of such a system is[18]

$$\alpha = \text{const}(E - E_{\text{gap}} - E_{\text{phonon}})^2, \qquad (1)$$

where E is the energy of light and E_{phonon} is the energy of the phonon that allows the shift in k space associated with the indirect transition.

We neglect the E_{phonon} term because Raman measurements have demonstrated that the highest energy of the phonons in NaCl-structured CdS is of the order of 0.05 eV.[2] If we assume that the Grüneisen parameter of CdS and CdSe is near one,[2,19] then we expect a maximum change of approximately 20%, or 0.01 eV, in phonon frequency, over the pressure range of these experiments. Additionally, neither our results nor previous band calculations[4] show any significant shift in the valence-band peaks or the conduction-band minima of either CdS or CdSe throughout this pressure range. Therefore, the phonons that enable the indirect transitions to occur are unlikely to change in character.

Representative absorption spectra of CdS are shown in Fig. 1. Although the spectra are generally quite similar, the energy gap values obtained from the extrapolation of the square root of absorption to zero absorption systematically decrease with compression (Fig. 2). The shift of the band gap of CdS with pressure is shown in Fig. 3. The shift follows a linear curve over this pressure range and is calculated to be
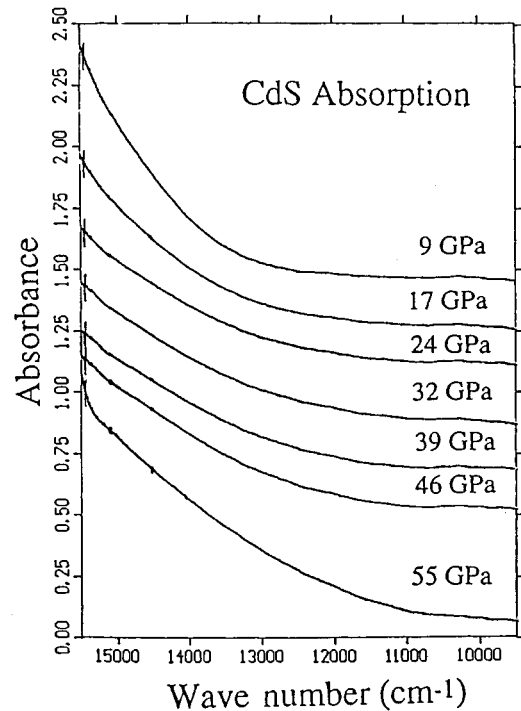

FIG. 1. CdS absorption spectra at high pressure. Absolute absorption values are displaced along the y axis for display purposes.

$-5.76(6) \times 10^{-3}$ eV/GPa. Previous measurements of the CdS band gap under pressure are consistent with our results (Fig. 3): Zhao *et al.*[2] used similar techniques to our own to measure rocksalt CdS energy gaps up to approximately 5 GPa. Savić and Urošević[3] measured energy gaps via photo-
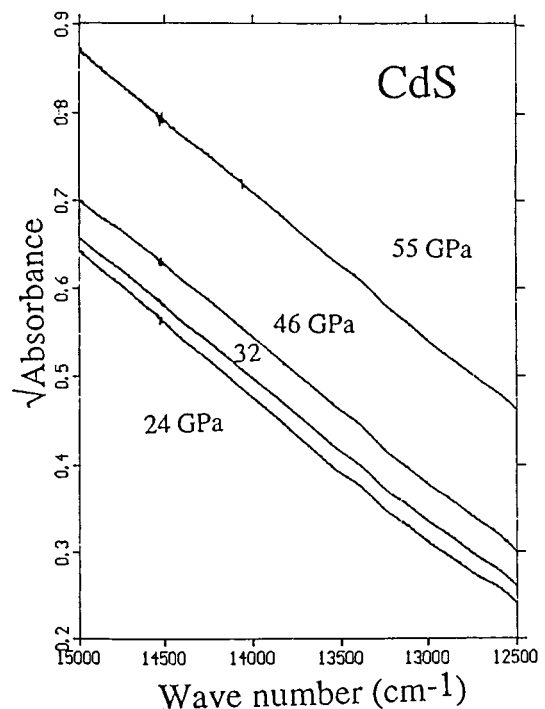

FIG. 2. Square root of CdS absorption for different pressures. The parallelism of these lines suggests that little broadening of the conduction-band minima occurs under compression.
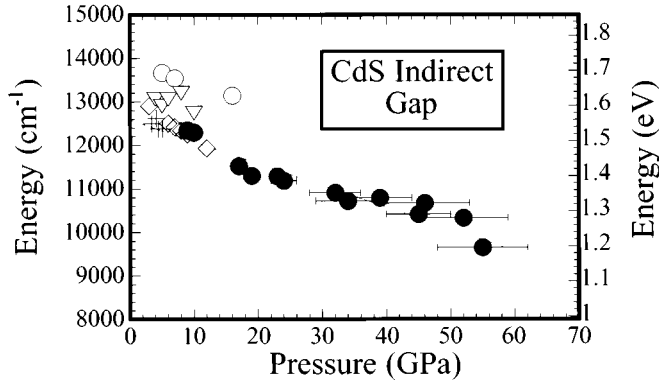
FIG. 3. Dependence of the CdS energy gap on pressure. The present measurements are shown with dark circles, while those of Edwards and Drickamer (Ref. 1) are shown with open circles, Batlogg *et al.* (Ref. 11) with inverted triangles, the photoconductivity measurements of Savić and Urošević (Ref. 3) with open diamonds, and the absorption data of Zhao *et al.* (Ref. 2) with crosses.

conductivity and their results are also in excellent agreement with our data, as are the optical absorption measurements of Batlogg *et al.*[11] to approximately 10 GPa. The earlier measurements of Edwards and Drickamer[1] are recalibrated in pressure using current value for pressure fixed points;[20,21] the trend of these data is in reasonable agreement with our measurements, but the absolute values of the gap are shifted to higher energy by 800 cm^{-1}, or 0.1 eV. This systematic shift is likely to be a consequence of the extrapolation of their data to a fixed absorption coefficient rather than the zero absorbance base line used in subsequent studies.

The observed shift in the gap is monotonic with pressure and our results are thus consistent with the transition remaining from the **L** point of the valence band to the **X** point of the conduction band throughout this pressure range. This contrasts with previous inferences[11] based on band-structure calculations[22] that a shift to a $\Sigma \rightarrow X$ transition may take place in CdS near 10 GPa. To evaluate further whether such a shift in the band structure of CdS might occur, we conducted theoretical electronic band-structure calculations using a pseudopotential approach[23] and density-functional theory in the local-density approximation[24] (LDA) with a plane-wave basis.[25] In order to study the effects of the cadmium $4d$ electrons on the band structure, we perform two calculations: one treats these electrons as part of the valence complex and the other considers them as part of the core. In the first calculation, we use Martins-Troullier-Wei pseudopotentials[26] and an energy cutoff of 50 Ry. In the second calculation, a Hamann-Schlüter-Chiang pseudopotential[27] with a partial core correction[28] is used for the cadmium atom and the energy cutoff is set to 60 Ry. Ten special k points are generated according to the Monkhorst-Pack scheme.[29] The exchange-correlation energy is calculated using the Ceperley-Alder interpolation formula.[30] Pressures are determined from the calculated volumes using the experimental equation of state for CdS of Suzuki *et al.*[31] and a Birch-Murnaghan equation of state. The calculated band structure for the rocksalt phase of CdS at 10 GPa is presented in Fig. 4. LDA calculations are known to underestimate band gaps or even to predict semimetallic band structure for small gap semiconductors. The band structure in Fig. 4 has no gap,
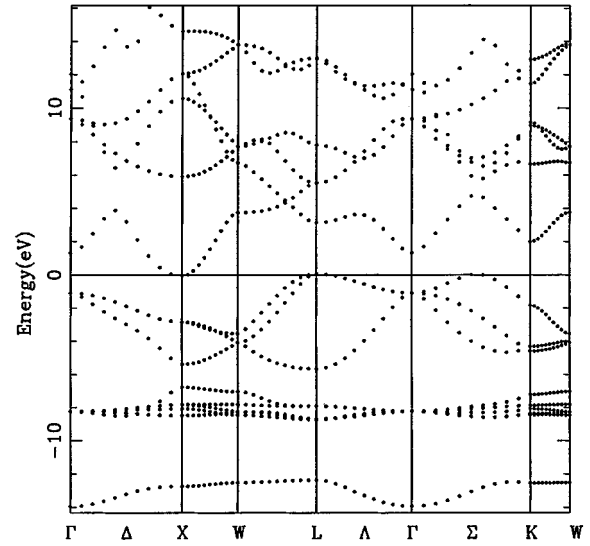

FIG. 4. Theoretical electronic band structure at 10 GPa for CdS calculated using valence d electrons. Zero energy is defined to be the maximum of the valence band.

although CdS at this pressure is known to be a semiconductor. Despite the fact that the absolute LDA values of gaps are incorrect, their pressure dependence is expected to be in reasonable agreement with experiment.[32,33]

The role of d electrons in determining the location and pressure dependence of the valence band is illustrated in Fig. 5. If d electrons are included in the pseudopotential core, the band gap of CdS exhibits a positive pressure shift. In contrast, when valence d electrons are included in the calculation, the pressure shift of the gap becomes negative (Fig. 5). This change in behavior is due to hybridization of the d
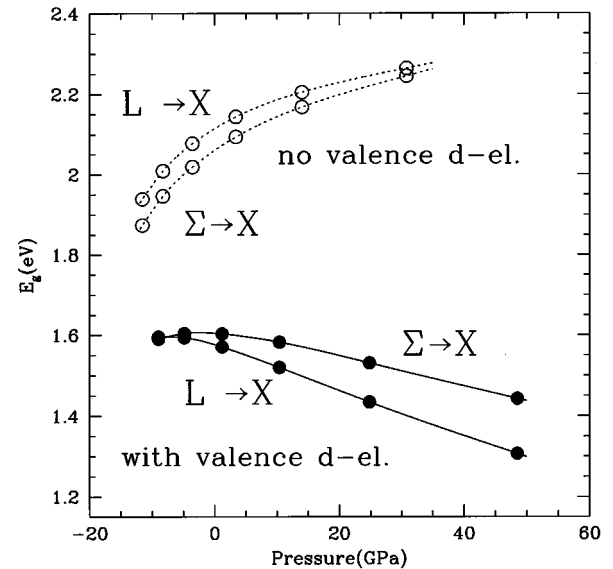

FIG. 5. Pressure dependence of the indirect calculated gaps for CdS in the rocksalt structure. The broken lines represent the calculations with Cd $4d$ electrons kept in the core and the solid lines with Cd $4d$ electrons in the valence complex. The value of the **L**$\rightarrow$**X** gap with valence d electrons at 10 GPa arbitrarily is taken to be equal to the experimental value of 1.5 eV.
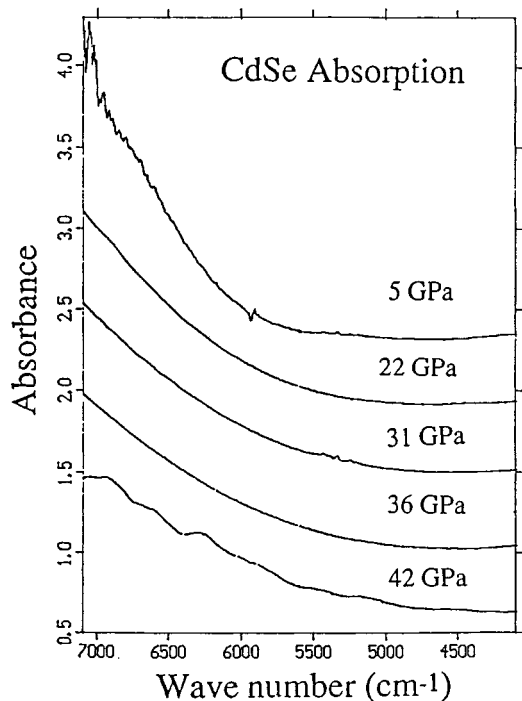
FIG. 6. CdSe absorption spectra under pressure. Spectra are displaced in absorption for clarity. The spectra at higher pressure show significantly more complex structure than those at low pressure, which may be due to pressure-gradient related defects.
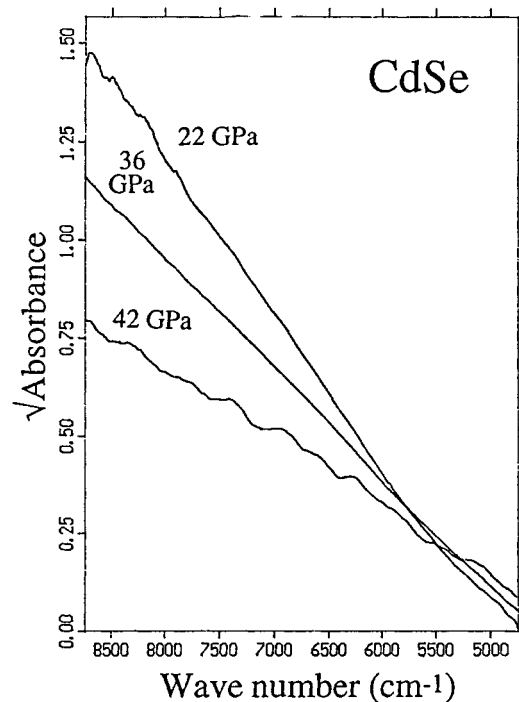

FIG. 7. Square root of the CdSe absorption spectra at different pressures. The lack of parallelism indicates that the conduction-band minima may broaden under compression.

levels with the upper valence-band levels and resultant level repulsion that pushes the **L** and **Σ** valence peaks up without affecting the conduction band at **X**, thus considerably reducing the gap. Since this effect becomes stronger at smaller volumes, the gap decreases with increasing pressure. As with previous calculations on CdSe,[4] the present results illustrate the profound effect that d-electron relaxation has on the calculated band structures of the chalcogenides.

The **L**→**X** slope determined from the theoretical calculation is in very good agreement with our experimental values. The calculated slope of -5.6×10^{-3} eV/GPa is consistent with our experimental value of $-5.7(6) \times 10^{-3}$ eV/GPa. Moreover, the **L**→**X** line decreases in energy more rapidly than the **Σ**→**X** line (Fig. 5); thus the **L**→**X** gap appears to remain the lowest-energy gap across the entire pressure range to 55 GPa. This lack of change in character for the indirect gap is in good accord with our experimental observations.

CdSe absorption spectra are shown in Fig. 6. In this material, some absorption was observed near 3000 cm^{-1}, which may be defect related. This phenomenon is not well understood, but may be due to pressure-gradient-induced defects in the sample. Our CdS results in alcohol had a similar background structure, while our data with lower-pressure gradients showed no such structure.

The energy gap values were obtained in the same way as for CdS, with similar square root of absorbance trends as shown in Fig. 7. Clearly, Fig. 7 illustrates that the constant term of Eq. (1) increases with pressure in CdSe. This effect is considerably more pronounced in CdSe than in CdS (compare Figs. 2 and 7) and is probably due to pressure-induced broadening of either the valence-band maxima or the conduction-band minima.

The pressure dependence of the band gap of CdSe derived from our measurements is, as with CdS, linear with pressure and the slope of the energy gap shift is determined to be $-4.0(2) \times 10^{-3}$ eV/GPa (Fig. 8). This result is in reasonable accord with the theoretical calculation of -6.0×10^{-3} eV/ GPa of Zakharov, Rubio, and Cohen.[4] Both our present results and the theoretical study are in disagreement with the older measurements of Edwards and Drickamer[1] of -1.5×10^{-2} eV/GPa (Fig. 8). Even when recalibrated with modern fixed point values,[20] the slope of Edwards and Drickamer's[1] measurements is only minimally altered. We have no simple explanation for the discrepancy between these measurements, particularly since the shift of E_{gap} with pressure for CdS from Ref. 1 is in excellent agreement with our data (Fig. 3).
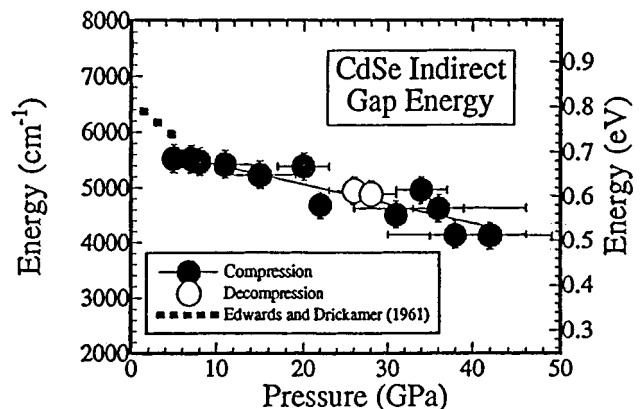

FIG. 8. Dependence of the CdSe energy gap on pressure; present measurements are shown as dark circles. The data of Edwards and Drickamer (Ref. 1) are shown by diamonds.

Neither CdS nor CdSe metallizes over the pressure range of our data; they remain indirect-gap semiconductors throughout our range of volumetric compaction. This result is in accord with the conductivity measurements of Ignatchenko and Babushkin[6] on CdSe to 50 GPa. If we make the simple assumption that the linear pressure shifts of the gaps persists, we predict that NaCl-structured CdS will metallize near 290 GPa. However, the diffraction data of Suzuki et al.[31] indicate that a transformation to a high-pressure polymorph, which may be orthorhombic in structure, occurs near 56 GPa. CdSe is predicted to metallize near 180 GPa, although it is theoretically predicted that the CsCl-structure becomes energetically favorable near 94 GPa.[4] It thus appears that, as with other rocksalt-structured chalcogenides (e.g., CaS, CaSe, BaS, and ZnS),[5,9,34] neither CdS nor CdSe will metallize in the rocksalt structure. Indeed, it appears that the gap between p-orbital-derived anion states and s- or d-orbital-derived cation states in these chalcogenides remains large and closes too slowly with pressure to produce metallization. This is particularly the case because the rocksalt-structured phase of these chalcogenides probably becomes structurally unstable prior to the pressure at which metallization is expected.

IV. CONCLUSION

The pressure coefficient dE_{gap}/dp for CdSe was determined to be $-4.0(2) \times 10^{-3}$ eV/GPa, while that of CdS is $-5.7(6) \times 10^{-3}$ eV/GPa. Each of these values is in reasonable agreement with theoretical predictions of -6.0×10^{-3} eV/GPa for CdSe (Ref. 4) and our calculation of -5.6×10^{-3} eV/GPa for CdS. For CdSe, our experimental results are in much better agreement with the theoretical value than the earlier results of Edwards and Drickamer,[1] indicating that this theoretical approach is able to predict the volume dependence of indirect-gap energies with reasonable accuracy.

Both CdSe and CdS rocksalt phases continue to have indirect gaps up to pressures of 42 and 55 GPa, respectively. From the continuous change in gap energies, both compounds appear to have gaps corresponding to $\mathbf{L} \rightarrow \mathbf{X}$ transitions throughout these pressure ranges, with no fundamental change in band structures observed in either the experimental or theoretical results. From the pressure shifts of the gap energies, it is predicted that CdS will metallize above 250 GPa, while CdSe will metallize above 150 GPa. In effect, this implies that metallic NaCl-structured CdS and CdSe probably will not exist; CdS appears to undergo a phase transition near 56 GPa (Ref. 31) and CdSe is theoretically predicted to favor the CsCl-structure near 94 GPa.[4] Thus it appears that these chalcogenides are unlikely to exist as NaCl-structured metals: the rate of pressure-induced gap closure in these phases, coupled with their generally large initial band gaps, indicates that structural instabilities are likely to occur at significantly lower pressures than those at which metallization is expected.

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